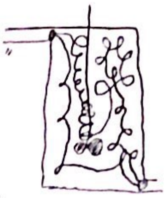
① Segregated flow model

- Basic Assumption and its consequences
  - → "the various fluid elements move through the reactor at different speeds without mixing one another"
  - → i.e., they remain segregated
  - → we can visualize each fluid element
    - → as a batch reactor
    - → operating at constant P
    - → with holding time equal to the correspondin Residence time for that fluid element.
  - → Because there is a distribution of Residence time for various fluid elements, the degree of conversion achieved within each fluid element is different and depends on its Residence time.



Average Conversion at exit stream $= \sum_{\text{all fluid elements}} \left(\begin{array}{c}\text{fractional}\\ \text{conversion}\\ \text{for Residence}\\ \text{time } t\end{array}\right) \times \left(\begin{array}{c}\text{fraction of fluid}\\ \text{elements with Residence}\\ \text{time between } t \text{ and } t+\Delta t\end{array}\right) \Longrightarrow \boxed{\bar{X} = \sum x(t).E(t).dt}$

or in integral form → $\boxed{\bar{X} = \int_0^\infty x(t).E(t)dt}$

- Hence, to evaluate $\bar{X}$, the average fractional conversion we need
  - → $x(t)$
    - → fractional conversion as a function of Residence time
    - → from rxn kinetics
  - → $E(t)$
    - → RTD function
    - → experimentally measured

- Ex. 01
  - → $\bar{X}$ and $x(t)$ for given kinetics
  - → consider a first order liquid phase irreversible rxn: $A \xrightarrow{k_1} B$, $k = 3.33 \times 10^{-3}\ s^{-1}$, $-r_A = kC_A$
  - → Estimate the conversion if the rxn is to be carried out in a Non-Ideal reactor for which RTD was measured from the following pulse experiment

- Solution of Ex. 01
  - → we can treat each fluid element as a small batch reactor (CVBR)
  - → Design eq. for a CVBR:

$$-r_A = -\frac{1}{V}\frac{d(C_A V)}{dt} \Rightarrow kC_A = -\frac{dC_A}{dt} \Rightarrow kC_{A_0}(1-x_A) = C_{A_0}\frac{dx_A}{dt} \Rightarrow \frac{dx_A}{1-x_A} = k\,dt$$

$$\xrightarrow{\text{integrating}} -\ln(1-x_A)\Big|_0^{x_A} = kt \Rightarrow 1-x_A = \exp(-kt) \Rightarrow \underline{x_A(t) = 1-\exp(-kt)}$$

  - → we can estimate $E(t) = \dfrac{c(t)}{\int_0^\infty c(t)dt} = \dfrac{c(t)}{\sum_0^\infty c(t).\Delta t}$, $\bar{X} = \int_0^\infty x(t).E(t).dt = \sum_0^\infty x(t).E(t).\Delta t$, $\Delta t = 120^s$

time $^{(s)}$	$c(t)$ (mol/m^3)	$c(t).\Delta t$ $(mol.s/m^3)$	$E(t) = \frac{c(t)}{\sum c(t).\Delta t}$	$x(t) = 1-\exp(-kt)$	$x(t).E(t).\Delta t$
0	0	0	0	0	0
120	6.5	780	1.083×10^{-3}	0.3294	0.0428
240	12.5	1500	2.083×10^{-3}	0.5503	0.1375
360	12.5	1500	2.083×10^{-3}	0.6984	0.1746
480	10.0	1200	1.667×10^{-3}	0.7978	0.1596
600	5.0	600	8.333×10^{-4}	0.8649	0.0869
720	2.5	300	4.167×10^{-4}	0.9091	0.0459
840	1.0	120	1.667×10^{-4}	0.9390	0.0188
960	0	0	0	0.9591	0
1080	0	0	0	0.9726	0

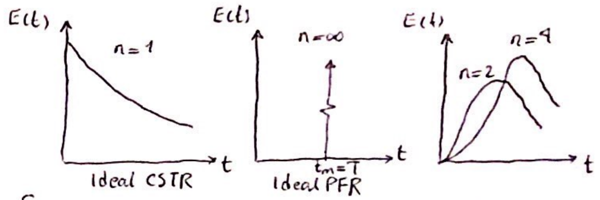
$\sum c(t).\Delta t = 6000$

$\bar{X} = \sum x(t).E(t).\Delta t$
$= \boxed{0.665}$

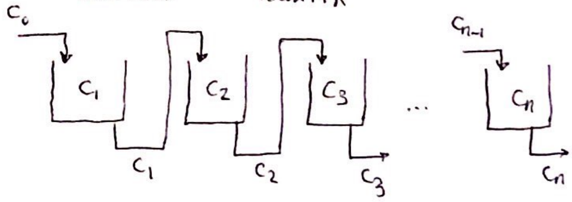
- Note
  - → we are using RTD function, $E(t)$, directly to obtain the fractional conversion
  - → for different rxn kinetics (e.g. reversible, irreversible, series, etc.) the functional form of $x(t)$ would be different.

② Tanks in series Model

- Recall that $\longrightarrow$ the performance of n equal size CSTR in series approaches that of a single PFR of the same total V as $n \to \infty$
- Hence
  - $\longrightarrow$ we can in some cases, characterize the observed RTD behavior of a real reactor in terms of n CSTR in series
  - $\longrightarrow$ for a real reactor, RTD behavior can fall between two extremes, $n=1$, and $n=\infty$
  - $\longrightarrow$ Objective: given RTD $\Rightarrow$ get n
  - $\longrightarrow$ Now, to develop RTD for CSTR in series



- Let us consider
  - $\longrightarrow$ n equal size CSTR in series
  - $\longrightarrow$ liquid phase (constant ν for each tank)
  - $\longrightarrow$ hence, $\tau_1 = \tau_2 = \tau_3 = \dots = \tau_n$
  - $\longrightarrow$ A pulse tracer test, where @ $t=0$; $C_1 = C_0$
  - $\longrightarrow$ General mole balance:



in − out + generation − consumption = accumulation

$$\begin{cases} 1^{st}\text{ tank}: & 0 - \nu C_1 = V_1 \dfrac{dC_1}{dt} \\ 2^{nd}\text{ tank}: & \nu C_1 - \nu C_2 = V_2 \dfrac{dC_2}{dt} \\ & \vdots \\ n^{th}\text{ tank}: & \nu C_{n-1} - \nu C_n = V_n \dfrac{dC_n}{dt} \end{cases} \xrightarrow[\text{CSTR}:\ \tau_i = V_i/\nu]{\text{for constant } \nu \text{ and equal size}} \begin{cases} 1^{st}\text{ tank}: & -C_1 = \tau_1 \dfrac{dC_1}{dt} \\ 2^{nd}\text{ tank}: & C_1 - C_2 = \tau_2 \dfrac{dC_2}{dt} \\ & \vdots \\ n^{th}\text{ tank}: & C_{n-1} - C_n = \tau_n \dfrac{dC_n}{dt} \end{cases}$$

τ_i is for CSTRs

- integrating first eq. using IBC $\Rightarrow$ $C_1 = C_0 \cdot \exp(-t/\tau_i)$
- for the second eq. $\Rightarrow$ $C_0 \cdot \exp(-t/\tau_i) - C_2 = \tau_2 \dfrac{dC_2}{dt} \Rightarrow C_2 = \dfrac{C_0 t}{\tau_i} \cdot \exp(-t/\tau_i)$
- Similarly: $\Rightarrow$ $C_n = \dfrac{C_0 \cdot t^{n-1}}{(n-1)\tau_i^{n-1}} \exp(-t/\tau_i)$
- $\displaystyle\int_0^\infty C_n(t)\,dt = \int_0^\infty \frac{C_0 \cdot t^{n-1}}{(n-1)\tau_i^{n-1}} \cdot \exp(-t/\tau_i)\,dt = \frac{C_0}{(n-1)\tau_i^{n-1}} \int_0^\infty t^{n-1} \cdot \exp(-t/\tau_i)\,dt$

$$= \frac{C_0}{(n-1)\tau_i^{n-1}} \left(-\tau_i \cdot \exp(-\tfrac{t}{\tau_i})\right)\left[t^{n-1} + (n-1)\tau_i t^{n-2} + (n-1)(n-2)\tau_i^2 t^{n-3} + \dots + (-1)^{n-1} \cdot (n-1)!\, \tau_i^{n-1}\right]_0^\infty = C_0 \tau_i (n-2)!$$

- $E(t) = \dfrac{C_n(t)}{\int_0^\infty C_n(t)\,dt} = \dfrac{\frac{C_0 \cdot t^{n-1}}{(n-1)\tau_i^{n-1}} \exp(-t/\tau_i)}{C_0 \tau_i (n-2)!} \Rightarrow \boxed{E(t) = \dfrac{t^{n-1}}{(n-1)!\,\tau_i^{n}} \cdot \exp(-\tfrac{t}{\tau_i})}$

- The important question is that suppose we have measured RTD for a given reactor and we want to model the reactor as n CSTR in series. How can we use RTD measurements to obtain n.
  - let $\tau = \dfrac{V_{total}}{\nu_0} = \dfrac{nV_i}{\nu_0} = n\tau_i \Rightarrow \tau_i = \dfrac{\tau}{n}$ ⤳ τ is for the real reactor

    where $\tau = t_m$ = mean residence time corresponding to the total V
  - $E(t) = \dfrac{t^{n-1}}{(n-1)!\left(\frac{\tau}{n}\right)^{n-1}} \cdot \exp(-\tfrac{nt}{\tau})$ ⤳ n (??)
  - $\displaystyle \sigma^2 = \int_0^\infty (t - t_m)^2 \cdot E(t)\,dt = \int_0^\infty \frac{(t-\tau)^2 \cdot t^{n-1} \exp(\frac{-nt}{\tau})}{(n-1)!\,(\frac{\tau}{n})^n} = \frac{1}{(n-1)!(\frac{\tau}{n})^n}\left[\underbrace{\int_0^\infty t^{n+1} \cdot \exp(\tfrac{-nt}{\tau})\,dt}_{=\mathrm{I}} - \underbrace{\int_0^\infty 2\tau \cdot t^n \exp(\tfrac{-nt}{\tau})\,dt}_{=\mathrm{II}} + \underbrace{\int_0^\infty \tau^2 t^{n-1} \cdot \exp(\tfrac{-nt}{\tau})\,dt}_{=\mathrm{III}}\right]$

$$= \frac{1}{(n-1)!(\frac{\tau}{n})^n}\left[(n+1)!\left(\frac{\tau}{n}\right)^{n+2} - 2\tau\left(\frac{\tau}{n}\right)^{n+1} \cdot n! + \tau^2\left(\frac{\tau}{n}\right)^n \cdot (n-1)!\right] = n(n+1)\left(\frac{\tau}{n}\right)^2 - 2\tau\left(\frac{\tau}{n}\right)n + \tau^2$$

$$= \left(\frac{n+1}{n}\right)\tau^2 - 2\tau^2 + \tau^2 = \tau^2\left(\frac{n+1}{n} - 1\right) = \tau^2\left(\frac{n+1-n}{n}\right) \Rightarrow \boxed{\sigma^2 = \frac{\tau^2}{n}} \quad \text{or} \quad \boxed{n = \frac{\tau^2}{\sigma^2}}$$

- If we want to model a reactor as n-tanks in series $\longrightarrow$ we can assume $\left.\begin{matrix} t_m = \tau \\ \sigma^2 \end{matrix}\right\} \Rightarrow \boxed{n = \dfrac{t_m^2}{\sigma^2}}$

- Recall that for n CSTR in series (each, of equal V), for 1^{st} order, irreversible, liquid phase rxn we have:

$$\frac{C_{A0}-C_{A1}}{\tau_1}=kC_{A1}\ ,\quad \frac{C_{A1}-C_{A2}}{\tau_2}=kC_{A2}\ ,\quad \frac{C_{A2}-C_{A3}}{\tau_3}=kC_{A3}\ ,\quad \cdots\ ,\quad \frac{C_{An-1}-C_{An}}{\tau_n}=kC_{An}$$

$$\frac{C_{A1}}{C_{A0}}=\frac{1}{1+k\tau_1}\ ,\quad \frac{C_{A2}}{C_{A1}}=\frac{1}{1+k\tau_2}\ ,\quad \frac{C_{A3}}{C_{A2}}=\frac{1}{1+k\tau_3}\ ,\quad \cdots\ ,\quad \frac{C_{An}}{C_{An-1}}=\frac{1}{1+k\tau_n}$$

- if $\tau_1=\tau_2=\tau_3=\cdots=\tau_n=\frac{\tau}{n}$ $\xrightarrow{\text{then}}$ $\frac{C_{An}}{C_{A0}}=\frac{1}{(1+k\frac{\tau}{n})^n}$

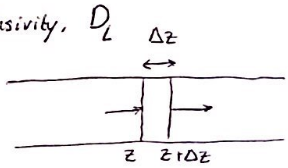
- $x_{An}=\frac{C_{A0}-C_{An}}{C_{A0}}=1-\frac{C_{An}}{C_{A0}}\Rightarrow x_{An}=1-\frac{1}{(1+k\frac{\tau}{n})^n}$

- Ex. 02 → Liquid phase reactor, 1^{st} order rxn, $k=0.1\ min^{-1}$, $t_m=10\ min$, $\sigma^2=24\ min^2$
  - → $n=\frac{t_m^2}{\sigma^2}=\frac{10^2}{24}=4.167$, $x_A=1-\frac{1}{(1+0.1\frac{10}{4.167})^{4.167}}\Rightarrow x_A=0.592$

- for other rate functions → e.g. 2^{nd} order, reversible, etc.
  - → we need to evaluate conversion at the exit of each reactor sequentially
  - → In the above case, find conversion for $n=4$, and 5, and interpolate

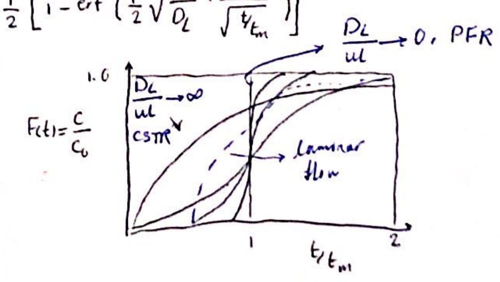
(3) Axial Dispersion Model

- Assumptions
  - → Plug flow with some degree of back mixing
  - → Deviation from plug flow is taken into account by an effective axial diffusivity, D_L



- MBE → for a non-reacting tracer injected into the reactor ($C \triangleq$ concentration of tracer)
  - $(F_{in}-F_{out})\Delta t=(CAV)\big|_{t+\Delta t}-(CAV)\big|_t$ (→ fluid velocity; → cross-sectional area)
  - → assuming constant volumetric flowrate $\dot{v}=uA_\phi$
  - → $F_{in}=\underbrace{\dot{v}C\big|_z}_{\text{by conv.}}+\underbrace{(-A_\phi D_L\frac{\partial C}{\partial z})\big|_z}_{\text{by diffusion}}$, and similarly $F_{out}=\dot{v}C\big|_{z+\Delta z}+(-A_\phi D_L\frac{\partial C}{\partial z})\big|_{z+\Delta z}$
  - → substituting in the MBE and taking the limit as $\Delta z\to 0$, we obtain: $\frac{\partial C}{\partial t}=D_L\frac{\partial^2 C}{\partial z^2}-u\frac{\partial C}{\partial z}$ (1)
  - → In dimensionless form → $\theta=\frac{t}{t_m}=\frac{tu}{L}$, $x=\frac{ut+z}{L}$
    - → eq. 1 becomes: $\frac{\partial C}{\partial \theta}=(\frac{D_L}{uL})\frac{\partial^2 C}{\partial x^2}-\frac{\partial C}{\partial x}$ (2)
    - → $\frac{D_L}{uL}$ → is called "Vessel dispersion No." which measures the extent of axial dispersion
      - → $\frac{D_L}{uL}\to 0$ ≡ negligible dispersion, plug flow
      - → $\frac{D_L}{uL}\to\infty$ ≡ large dispersion, CSTR

- Considering eq. 1 with a step input of tracer, C_0
  - → boundary conditions are
    - → $C=C_0$ @ $z=-\infty$, for $t\geq 0$
    - → $C=0$ @ $z=+\infty$, for $t\geq 0$
    - → $C=0$ @ $z>0$, for $t=0$
    - → $C=0C_0$ @ $z<0$, for $t=0$
  - → Solution procedure usually numerical
  - → but for small values of $\frac{D_L}{uL}$, an approximate analytical is as follows: $\left(\frac{C}{C_0}\right)_{step}=\frac{1}{2}\left[1-\text{erf}\left(\frac{1}{2}\sqrt{\frac{uL}{D_L}}\cdot\frac{1-t/t_m}{\sqrt{t/t_m}}\right)\right]$
  - → The dispersion model presupposes that the mixing state can be represented by a particular value of $\frac{D_L}{uL}$ (one that best fits the measured RTD)

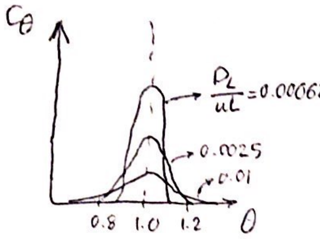


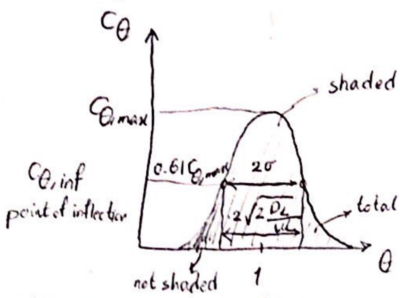
- for small values of $\frac{D_L}{uL}$, an approximate analytical solution for eq. 1, for a pulse input of C_c is given by:

$$t_m \left(\frac{C}{C_o}\right)_{pulse} = C_\theta = \frac{1}{2\sqrt{\pi \frac{D_L}{uL}}} \cdot \exp\left(-\frac{(1-t/t_m)^2}{4\frac{D_L}{uL}}\right)$$. which gives symmetrical C_θ curve

Q

- dimensionless units: $\theta = \frac{t}{t_m}$, $C_\theta = t_m C$, $C = \frac{c(t)}{C_o}$, $E_\theta = t_m E$, $\theta_m = 1$, $F_B = F$, $\sigma_\theta^2 = \frac{\sigma^2}{t_m^2}$





$\sigma_\theta^2 = 2\frac{D}{uL}$, $\sigma_\theta^2 = \frac{\sigma^2}{t_m^2}$

$t_m = \frac{L}{u}$

$\Rightarrow \sigma^2 = 2\left(\frac{DL}{u^3}\right)$ (Variance of c curve)

- $\frac{D_L}{uL}$ can be obtained from: variance, max height, width at the point of inflection

- For series of vessels → means and variances are additive
  - $\sigma^2_{overall} = \sigma^2_{vessel\,a} + \sigma^2_{vessel\,b}$
  - $t_{m,overall} = t_{m,vessel\,a} + t_{m,vessel\,b}$

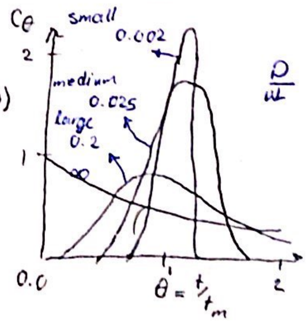
- The treatment presented so far
  - → was for small extent of dispersion, where an approximate analytical solution was used.
  - → Comparison with more complex but exact solutions indicate:

    error < 5% for $\frac{D}{uL} < 0.01$

    error < 0.5% for $\frac{D}{uL} < 0.001$
  - → furthermore, this treatment is valid for both open and closed vessel

  - closed vessel → Inlet and Outlet to vessel are plug flow
  - open vessel → " " " also have the same D as the vessel.

- For large extent of Dispersion
  - → Closed vessel + pulse input
    - → $\bar{\theta}_c = 1$
    - → $\sigma_\theta^2 = 2\frac{D}{uL} - 2\left(\frac{D}{uL}\right)^2 \cdot \left(1 - \exp\left(-\frac{uL}{D}\right)\right)$
    - → C_θ is obtained numerically



  - → Open vessel
    - → Analytical solution:
    - → $C_\theta = \frac{1}{2\sqrt{\pi\theta\left(\frac{D}{uL}\right)}} \cdot \exp\left[-\frac{(1-\theta)^2}{4\theta\left(\frac{D}{uL}\right)}\right]$
    - → $\bar{\theta}_c = 1 + 2\frac{D}{uL}$
    - → $\sigma_\theta^2 = 2\frac{D}{uL} + 8\left(\frac{D}{uL}\right)^2$

- See examples 3-5 from text. for calculation of $\frac{D}{uL}$ from RTD